Optimisation of Several Industrial and Recently Developed AJAM Naphtha Isomerization Processes Using Model Based Techniques

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Abstract

Increasing the yield and research octane number (RON) of naphtha isomerization process are the most important issues in industries. There are many alternative industrial naphtha isomerization processes practiced around the world. In addition, AJAM is a new naphtha isomerization process proposed by the authors recently (**Ahmed et al., [1]**) where the isomerization reactor model was validated using real data of Baiji North Refinery (BNR) of Iraq. In this work, first, the performance of the **AJAM** Process is evaluated against 8 existing industrial isomerization processes in terms of RON, yield and the cost using model based optimisation techniques. To be consistent, we have used the same isomerization reactor model in all the industrial processes we evaluated here. Secondly, energy saving opportunity in the new **AJAM** process is studied using pinch technology.

Key words: Izomerization Process and Technologies, Optimization, Mathematical Modeling

1. Introduction

Recently, increasing share of isomerizate was added to the gasoline pool as a result of the stringent environmental legislation which call for bring down utilization of aromatics and olefins in gasoline. In overall generation of car fuel in the world, perpetual tendency to the toughening of its environmental properties is noticed. Hence, the worldwide and local legislation to gasoline fuel impressively restrict the content of benzene, aromatic, olefin and sulfur compounds. Producing a clean gasoline fuel with high octane number in addition to

increasing the market demand for gasoline car fuel using a current simple naphtha isomerization technology is proved to be a very cost effective process. Thus, the improvement of isomerization process is one of the effective methods for the solution of such problem (i.e. increasing the quality (RON) and quantity (yield)) [2].

The once through operation of zeolitic isomerization process (without any recycle or by-pass) is economically efficient process and may be used with low cost to increase the RON of light naphtha, but the maximum value of RON that obtained is 80. However, such issue can be addressed by using recycle technology, by-pass technology or with the combination of both. Use of these technologies can increase the RON of light naphtha by more than 90 making an excellent component in gasoline pool [3].

The isomerization process technologies are widely used in refining applications, where light normal paraffins isomerization process is being considered recently. The reduction of benzene and limiting the aromatic and olefinic components in gasoline cause losses of the octane number in gasoline structure pool, thus the isomerization process has gained the attention to produce high octane branched paraffin's. The isomerization reactions are reversible reactions, so it is impossible to convert all low octane straight hydrocarbons chain to high octane branched hydrocarbons chain without improving the isomerization process. An environmental way for improving the quality of gasoline is through the production of branched paraffins from the normal paraffins, which can be carried out via light naphtha isomerization process having C5–C6 paraffins with taking into accounts the stringent legislations for advanced liquid fuels processing in petroleum refineries. In isomerization process, low octane paraffins are isomerized to produce a flexible high octane, free of sulfur, benzene and olefins feed stock. Also, the production of iso-butanes by isomerization process of normal butanes is again a popular application to deliver feed for alkylation process and chemical plants [4].

1.2 Scope of This Research

There are many isomerization processes in the world. Although the configuration of each of them varies depending on the existence of recycle or by-pass, the isomerization reactor is at the heart of each of these alternative processes. However, note that the catalysts used in such reactors and the process operating conditions vary depending on the ultimate goal. In this work, we evaluate the performance (RON, Yield and Cost) of all these configurations using model based optimisation techniques. For the reactor model in each of these industrial processes, we use our recently developed model [1]) which was validated using the

industrial data of Baiji North Refinery (BNR) of Iraq. The performances of all these alternative configurations are then compared with the performance of our recently developed configuration [1]. Finally, we look at the energy saving opportunity of the **AJAM** process using the Pinch Technology.

1.3 Novelty of this work

In our recent study [1], a detailed process model was developed for an existing naphtha isomerization reactor of Baiji North Refinery (BNR) of Iraq which involved estimation of the kinetic parameters of the reactor. The optimal values of these kinetic parameters were estimated based on BNR data and model based optimisation technique. A new isomerization process (named as **AJAM** process) was then proposed in **Ahmed et al.,** [1] using the reactor model developed. The main focus of this current paper is to evaluate the AJAM process against many other alternative industrial isomerization process technologies that have not been studied in [1] except the fact that comparison was only made between the **AJAM** process and the once through process. However, here, the industrial technologies such as hexorb, TIP, Ipsorb, DIH & DIP and DIH processes are used for the purpose of evaluating the **AJAM** process in terms RON and checking whether one of these industrial technologies can give higher RON or not. Also the productivity of the AJAM process in addition to the overall annual cost are compared with those obtained using these industrial technologies. Finally, opportunity for reducing the energy consumption and maximizing the heat recovery for the AJAM process is also investigated in this study by using the pinch technology.

The modelling, simulation and optimization processes of isomerization operations for all case studies in this work are carried out using **gPROMS** (**g**eneral **Pro**cess **M**odelling **S**ystem) software.

2. Alternative Isomerization Process Technologies

To achieve higher octane number several alternative isomerization process technologies have been developed over the years in which lower octane components are separated and recycled back into the reactors. Low RON components such as normal paraffin's are separated from the isomerizate and returned to the reactor feed. Many technologies such as distillation process and molecular sieve adsorption process or combination of them are used to separate normal paraffin's. Choice of the separation techniques is an important issue that mainly depends on the feed composition, desired RON and investment cost [3]. These alternative technologies are presented and described below:

2.1 **Once Through (OT) Process**

The once through process of Baiji isomerization unit is accomplished by Axens Company. This process is presented in Figure 1. The details of this process can be found in [1].

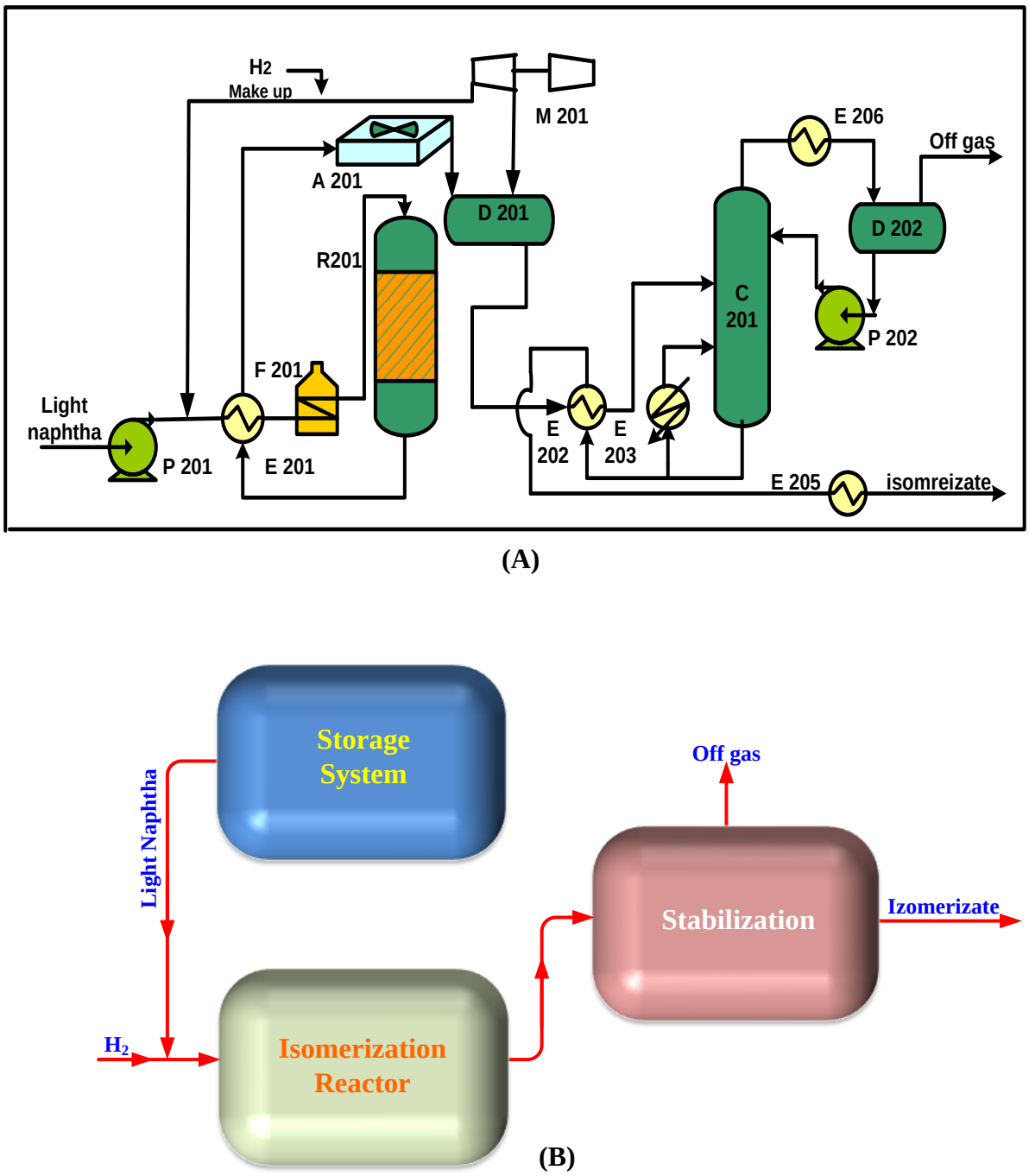

Figure 1: (A) Flow diagram of once through process (BNR) **(B)** Block diagram of OT process (BNR process)

2.2 **Deisopentanizer (DIP) Process**

In this isomerization scheme shown in Figure 2, distillation column is located before the reactor to separate Iso-pentane component from light naphtha feed to increase the normal pentane conversion. The downstream of the distillation enters to the isomerization process and such process was modified by adding stabilization process for the purpose of producing stabilized isomerizate and mixing with iso-pentane stream. This scheme becomes reasonable for the composition of iso-pentane in the feed with more than 13-15% [2, 3].

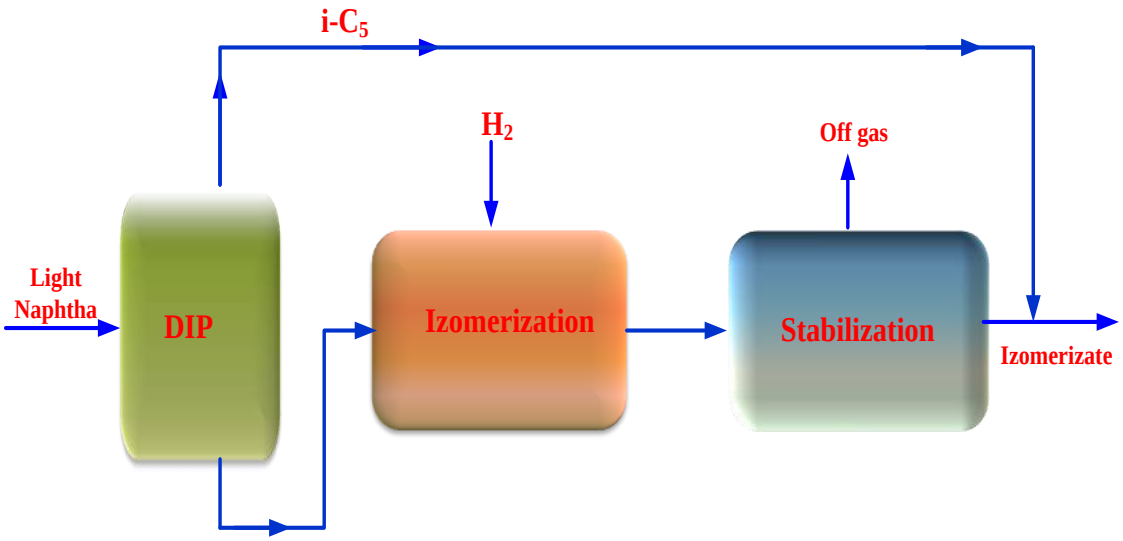

Figure 2: Block diagram of process with DIP

2.3 **Deisohexanizer (DIH) Process**

To increase the conversion of 2,2-Dimethyl butane (RON=94) and 2,3-Dimethyl butane (RON=105), normal hexane (RON=25), 2-methyl pentane (RON=74.4) and 3-methyl pentane (RON=75.5) are separated and recycled to the reactor. As shown in Figure 3, distillation column is used for separation process and 65% of the C_6-hydrocarbons are separated from product of isomerization unit stream and recycled to the reactor inlet stream. The column is located after stabilization process and the top product of distillation is stabilized the isomerizate [2, 5].

2.4 **DIP - DIH Process**

Using of DIP technology increases the conversion of normal pentane and there is no effect on the hexane conversion has observed. Also, the use of DIH increases the hexane conversion only. So, a combination between DIP and DIH is used to get high RON and yield

as shown in Figure 4. Tow distillation columns are used, the first one is located before the isomerization unit and working as DIP (explained in case 2). The second column is located after the isomerization unit and working as DIH (explained in case 3) [2, 5].

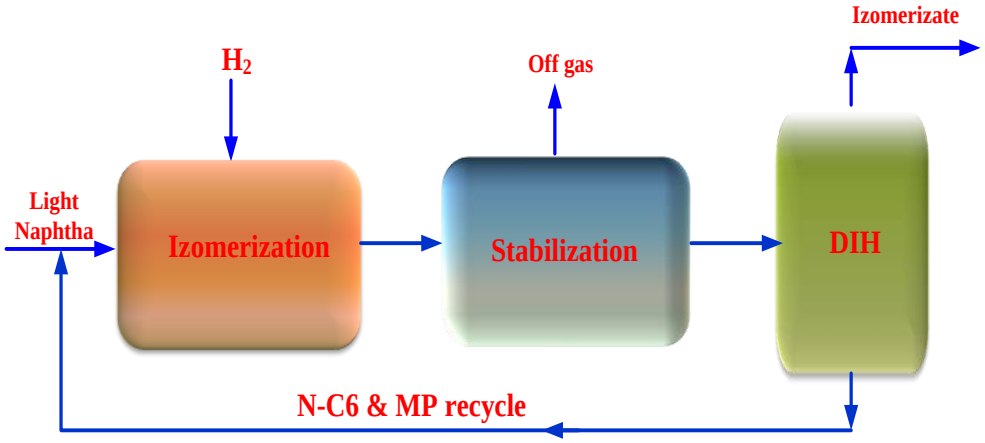

Figure 3: Block diagram of isomerization unit with DIH

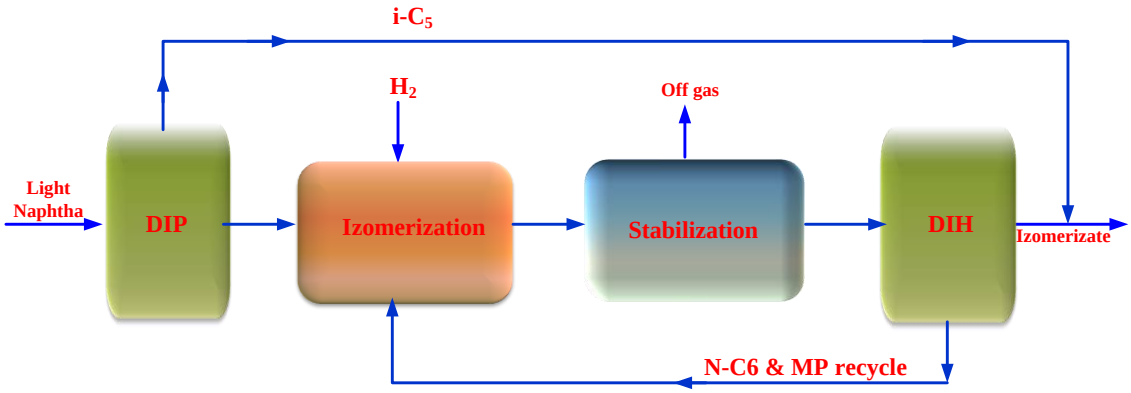

Figure 4: Block diagram of isomerization unit with DIH and DIP

2.5 **Ipsorb Process**

In this case (Figure 5), the adsorption of normal paraffin's (pentane and hexane) is used by molecular sieve adsorbers, followed by desorption from the pores and then they are recycled to the feed stock and the stream of iso-pentane is used to recover normal paraffins. This technology is developed by Axens and Zeolite 5A is used as a molecular sieve. Two adsorber columns, work alternately, are located after isomerization reactor system. Adsorption process acquires the same temperature and pressure of the reactor exit stream [3, 6].

2.6 **Hexorb Process**

In the case 6, as shown in Figure 6, the scheme combines between the molecular sieve and DIH technology, also in the Hexorb process all normal paraffins adsorb and convert to isomers. Here, methyl pentanes (RON 74.4 and 75.5) are recycled with normal paraffins due to add DIH after molecular sieve system. After isomerization process, reactor outlet stream enters into the adsorber column to separate normal paraffins. Branched paraffins pass through adsorber bed and enter to DIH to separate methyl pentane components that are recycled to the reactor. Before entering the reactor, stream of methyl pentane is used to recover the normal paraffins from adsorber bed and recycle to the reactor [4, 5].

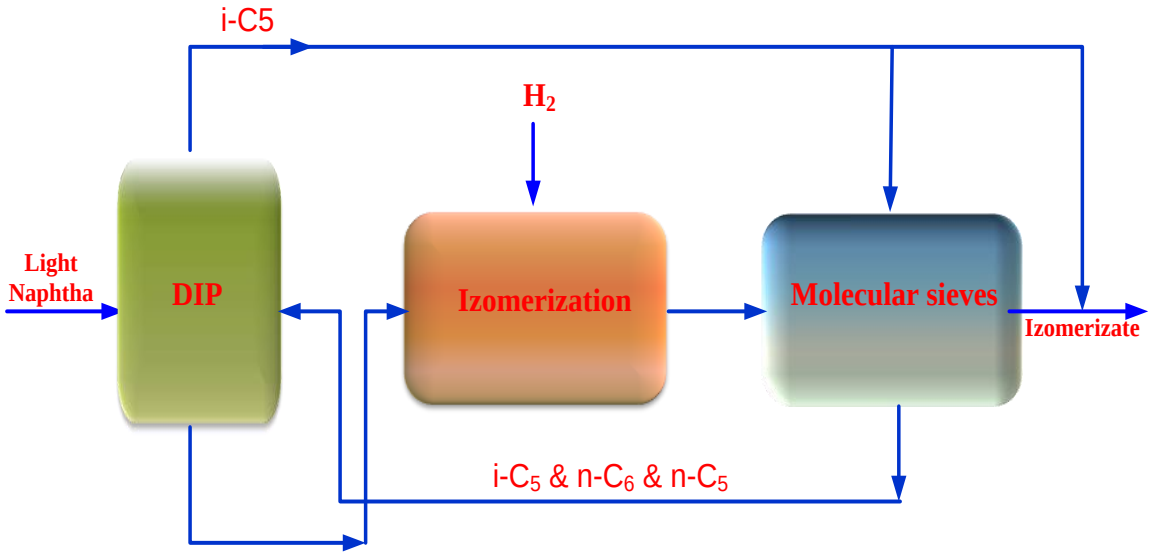

Figure 5: Block diagram of Ipsorb isomerization unit

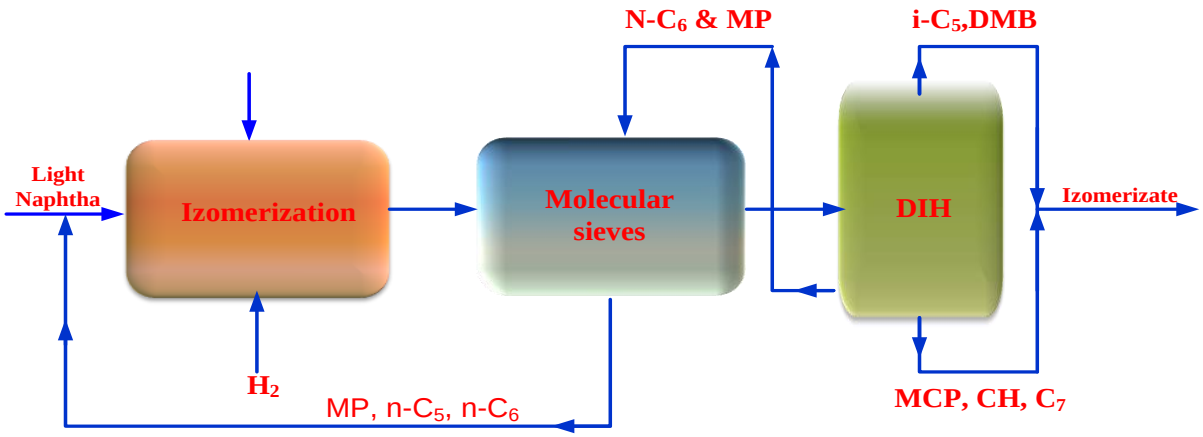

Figure 6: Block diagram of Hexorb isomerization unit

2.7 **Total Isomerization Process (TIP)**

UOP offers the isomerization process with molecular sieves adsorption system to separate and recycling the normal paraffins. In this scheme (Figure 7), after heating light naphtha stream, the stream is entered to the isomerization reactor. The product of the reactor is entered to the adsorption towers to separate the normal paraffins and recycle it to the reactor. The stream of hydrogen is used to recover the normal paraffins from adsorber column [7].

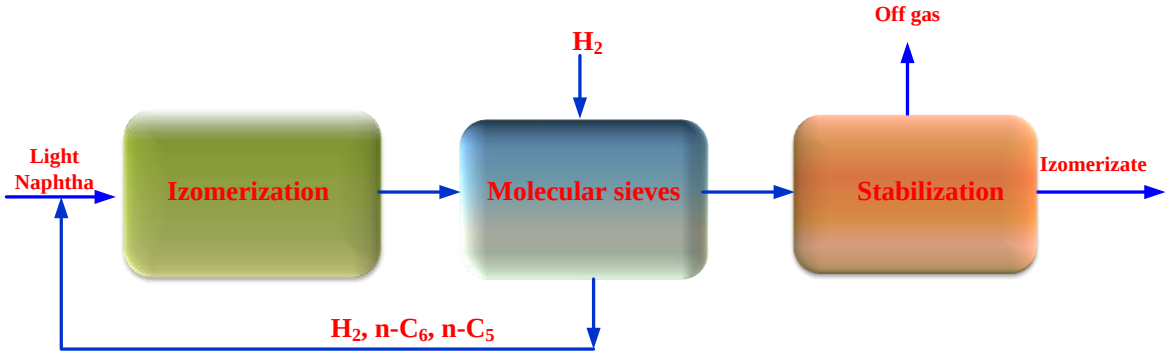

Figure 7: Block diagram of TIP isomerization unit

2.8 **AJAM Process**

Ahmed et al. [1] recently proposed this process as shown in Figure 8. They evaluated its performance against the OT process (Figure 1) for the Bajii North Refinery (BNR).

The high economic cost of molecular sieve technologies due to their high recycle rate leads to make a suitable modification on schemes of these technologies under reducing the economic cost with the same performance and to maximize RON. According to the specifications of naphtha feed stock at Baiji isomerization unit, the separation process can firstly be made owning to the content of benzene component. The new isomerization process proposed here is applied on the scheme of TIP as shown in Figure 8a,b. As firstly seems in this figure, the light naphtha stream is heated through heat exchanger (E201) and mixed with the reactor product stream and will be heated through the furnace F201befor entering to the adsorber S201. There are two adsorber columns work alternately. Through the adsorber S201, the normal paraffins are adsorbed by the molecular sieve and only branched paraffins leave the column. The normal paraffins remaining within adsorber S202 are desorbed by hydrogen stream (which is heated through the furnace F202 after compressed by Co201). The bottom stream of the adsorber S202 is entered to the reactor R201. The reactor product stream is condensed through E206 to separate the hydrogen from isomerizate stream within separator drum D201. Top product (hydrogen stream) of D201 is entered to Co201and the

bottom product (isomerizate) is heated through E206 before mixing with light naphtha stream. The top stream of S201 is condensed through E201 and then entered to stabilization zone. After that, branched paraffins are partially vaporized through E202 by heat exchange with the bottom product of the stabilizer. Light hydrocarbons (methane, ethane, propane and part of butane) are separated from the isomerizate as a top product. The bottom product of the stabilizer (isomerizate) cooled through E202 and E204 before the storage.

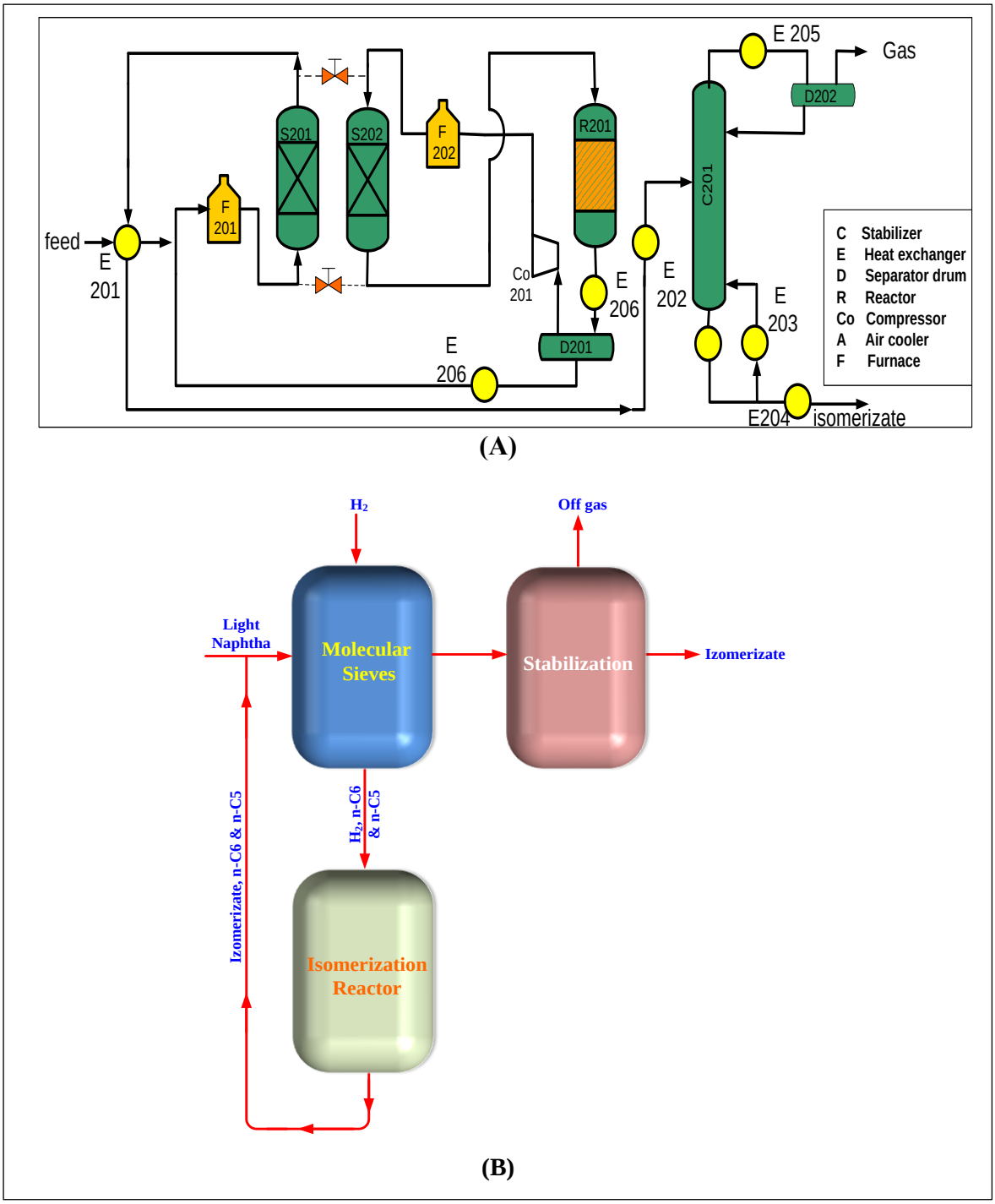

Figure 8 (A): Flow diagram of the **AJAM** isomerization process [1] **(B):** Block diagram of the **AJAM** isomerization process [1]

The recycle modes of operation can lead to product octane as high as 93 RON as shown in Table 1 [1]. Note, BNR uses Pt/Zeolite catalyst in their Once Through process. Table 2 below provides the review of the industrial isomerization processes and their performance (RON) with a brief description of operating condition, catalyst, and performance of isomerization unit at some refineries [4, 8].

Table 1: The RON of the isomerization process obtained by different technologies and catalysts [2]

Technology	**Pt/Zeolite**	**Pt/Al_2O_3**	**Pt/ZrO_2-SO_4**
Once Through (OT)	78-80	83	81-83
DIP	82	84	82-84
DIH	86	88	86-87
DIP and DIH	-	90-93	89-90
DIP, DIH and DP	-	-	91-92
TIP	87-90	-	91-92
Ipsorb	88	90	-
Hexorb	90	93	-
AJAM (**Ahmed et al., 2018** [1])	**90.72**	-	-

Table 2: Operating conditions and performance of different industrial isomerization processes in various refineries

Refinery	**Technology**	**Catalyst**	**Operating Conditions**	**RON of Isomerizate**	**The Licensing Company**
LUKOIL-Nizhegorodne-fteorgsintez	DIP	Sulfated zirconia	T= 160°C P=3.2 MPa LHSV= 2.5 hr^{-1}	86-87	UOP
Komsomolsky	DIP	Pt/Cl Al_2O_3	T=130 °C, P=3 MPa LHSV=2 hr^{-1}	86-88	Axens
Achinsky	DIH	Pt/Cl Al_2O_3	T=132 °C P=2.9 MPa	86-87	UOP
LUKOLL Volgogradnefte-pererabotka	DIP and DIH	Pt/Cl Al_2O_3	-	89-90	UOP
Saratovsky	DIP, DIH and DP	Pt/zeolite	-	91-92	SIE
Orsknefteor-Gsintez	Once-through	Pt/zeolite	-	80-82	SIE
Syzransky	DIP and DIH	Pt/zeolite	T=240 °C P= 2.7 MPa LHSV=3 hr^{-1}	89-90	Axens
Bajii	OT	Pt/zeolite	T=250 °C P= 2.4 MPa LHSV=1.6 hr^{-1}	78-80	Axens
-	**AJAM**	**Pt/zeolite**	**T=248 °C** **P= 2.1 MPa** **LHSV=1.5 hr^{-1}**	**90.81**	-

3. Isomerization Reactor Model for BNR (OT Process)

Ahmed et al. [1] described the development of the isomerization reactor model based on real industrial data of BNR in detail. For the convenience of the reader it is summarized here. Isomerization unit of BNR is an once through mode based on zeolitic catalyst system. As shown in Figure 1a,b, light naphtha obtained by hydrotreating process is mixed with compressed hydrogen before entering heat exchanger one (E-201), which rises the temperature of the feed to 190ºC.

The furnace F-201 provides the proper level of temperature to the reactor R-201 inlet. The isomerisation chemical reactions take place into the reactor R-201 (as cylindrical with a height of 13.840 m and diameter of 2.9 m) loaded with a bed of catalyst IP 632. The reactor effluent is partially condensed through E-201, the air condenser A-201 and the trim cooler E-202 before feeding it to the high pressure separator drum D-201 and the overhead stream (which is hydrogen) is compressed and recycled to the reactor. The liquid taken from drum D-202 is heated through heat exchanger E-202 to provide the required inlet column temperature of C-201. The head stream is partially condensed by heat exchanger E-204 then enters into the separator D-202. The downstream of C-201 is cooled through E-202 and then by E-205 to produce stabilized isomerizate.

4. Optimization of Industrial Processes

Here, we carry out process optimization of all the industrial processes presented in section 2. Note, in each of these technologies, the isomerization reactor model is same as that of BNR process developed and validated recently by **Ahmed et al [1]**. Thus, the catalyst used for the reactor is also same (Table 2 shows 4 out 8 industrial processes use this catalyst). It is for making a fair comparison of performances between them.

4.1 **Mathematical Model**

The mathematical model used is presented in appendix A and can also be found in [1].

4.2 **Energy Balance**

Energy balance on heat transfer equipment is essential to estimate the area of heat transfer (A_t) and heat duty (Q_F) as a function of temperatures. The stream temperatures of once through, DIP, DIH, Ipsorb and Hexorb configurations are the same with those used in the isomerization unit at Baiji refinery (presented in Table 3). But, for TIP and the **AJAM** processes, the streams temperatures (presented in Table 4) were taken from **Holcombe [7]**.

Heat capacities of liquid naphtha were taken from **Gary at el [9]**, heat transfer coefficient was taken from **Douglas [10]**. All these parameters are presented in Tables 3 and 4.

Table 3: Values of coefficients and constant parameters used in one through, DIP, DIH, Ipsorb and Hexorb configurations

Parameter	Unit	Value	Parameter	Unit	Value
$\boldsymbol{T1_{o,h}, T2_{o,h}}$	K	60	U_2	kW/m^2	0.387
$\boldsymbol{T1_{i,c}}$	K	43	U_3	kW/m^2	0.942
$\boldsymbol{T2_{i,c}, T4_{o,c}}$	K	40	U_4, U_5	kW/m^2	0.4
$\boldsymbol{T2_{i,h}}$	K	169	λ_{c1}	kJ/kg	274
$\boldsymbol{T2_{o,c}}$	K	132	λ_{h1}	kJ/kg	268
$\boldsymbol{T3_{h}}$	K	200	λ_{c2}	kJ/kg	317
$\boldsymbol{T4_{o,h}}$	K	20	$Cp_{h1,l}$	kJ/kg.k	2.531
$\boldsymbol{T4_{i,c}}$	K	16	$Cp_{c1,l}$	kJ/kg.k	2.522
$\boldsymbol{T1_{b,h}, T1_{b,c}}$	K	450	$Cp_{c2,l}$	kJ/kg.k	2.481
$\boldsymbol{T2_{b,c}}$	K	386	$Cp_{l,4}$	kJ/kg.k	2.388
$\boldsymbol{U_1}$	kW/m^2	0.432	$Cp_{l,5}$	kJ/kg.k	2.388

Table 4: Values of streams temperatures, coefficients and constant parameters used in TIP and ACP configurations

Parameter	Unit	Value	Parameter	Unit	Value
$\boldsymbol{T1_{o,h}, T2_{o,h}, T3_{o,h}}$	K	333	U_2	kW/m^2	0.432
$\boldsymbol{T1_{i,c}, T2_{i,c}, T3_{i,c}}$	K	313	U_3	kW/m^2	0.387
$\boldsymbol{T1_{o,c}}$	K	505	U_4	kW/m^2	0.913
$\boldsymbol{T2_{o,c}}$	K	537	U_5, U_6	kW/m^2	0.4
$\boldsymbol{T3_{i,h}}$	K	442	λ_{c1}	kJ/kg	274
$\boldsymbol{T3_{o,c}}$	K	405	λ_{h1}	kJ/kg	268
$\boldsymbol{T4_{i,h}, T4_{o,h}}$	K	463	λ_{c2}	kJ/kg	317
$\boldsymbol{T5_{i,c}, T6_{i,c}}$	K	288	$Cp_{h1,l}$	kJ/kg.k	2.531
$\boldsymbol{T5_{o,c}, T6_{o,c}}$	K	313	$Cp_{c1,l}$	kJ/kg.k	2.522
$\boldsymbol{T5_{i,h}, T6_{i,h}}$	K	333	$Cp_{c2,l}$	kJ/kg.k	2.481
$\boldsymbol{T5_{o,h}, T6_{o,h}}$	K	298	$Cp_{l,4}$	kJ/kg.k	2.388
$\boldsymbol{T_{o,f1}, T_{o,f2}}$	K	603	$Cp_{l,5}$	kJ/kg.k	2.388
$\boldsymbol{U_1}$	KW/m^2	0.432	$Cp_{l,6}$	kJ/kg.k	2.388

a) Energy Balance of Heat Exchanger E_{201} (Figure 8a)

Through this equipment, cold light naphtha is heating and vaporized as a result of the heat transfer from the hot stream of isomerizate as shown in Figure 9.

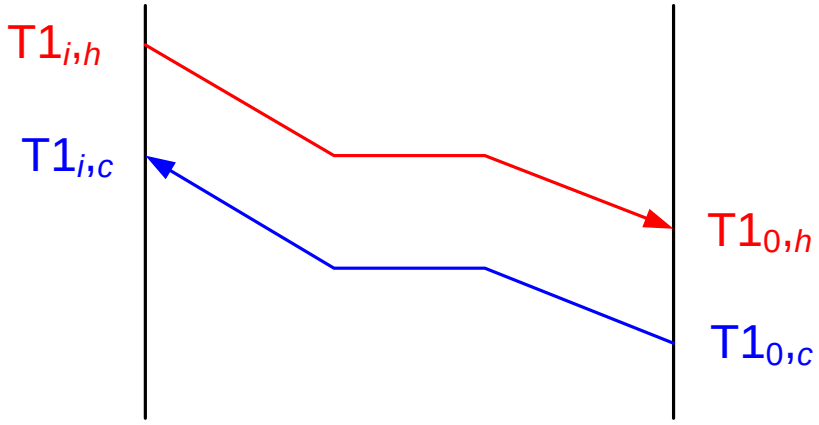

Figure 9: Heat exchanger E201

The area of heat transfer is calculated as a function of outlet reactor temperature, by the following equation:

$$A_{t1} = \frac{Q_{HE1}}{U_1 \Delta T_{lm1}} \quad \ldots(1)$$

$$\Delta T_{lm1} = \frac{\Delta T_{1,1} - \Delta T_{1,2}}{ln\left(\frac{\Delta T_{1,1}}{\Delta T_{1,2}}\right)} \quad \ldots(2)$$

$$\Delta T_{1,1} = T1_{i,h} - T1_{i,c} \quad \ldots(3)$$

$$\Delta T_{1,2} = T1_{o,h} - T1_{o,c} \quad \ldots(4)$$

Where:

$T1_{i,h}$: The inlet temperature of hot stream into E201, K

$T1_{i,c}$: The inlet temperature of cold stream into E201 K

$T1_{o,h}$: The outlet temperature of hot stream from the heat exchanger E201, K

$T1_{o,c}$: The outlet temperature of cold from heat exchanger1 (HE1), K

$$T1_{i,h} = T \quad \ldots(5)$$

T: The outlet reactor temperature, K (calculated from reactor energy balance equation).

$T1_{o,h}$ & $T1_{i,c}$ are given as constant values.

$T1_{o,c}$ is calculated as a function reactor outlet temperature T as follow:

Heat loss from hot stream = heat absorbed by cold stream

$$T1_{o,c} = \left(Q_{HE1} - W_{ln}\left(\lambda_{c1} + Cp_{c1,l}\left(T1_{b,c} - T1_{i,c}\right) + Cp_{c1,v}\, T1_{b,c}\right) + W_{H_2,in}\, Cp_{H2}\, T1_{i,c}\right) /$$
$$\left(W_{H_2,in}\, Cp_{H2} + W_{ln}\, Cp_{c1,v}\right) \quad \ldots(6)$$

$$Q_{HE1} = W_{iso}\left(\lambda_{h1} + Cp_{h1,l}\left(T1_{b,h} - T1_{i,h}\right) + Cp_{h1,v}(T1_{o,h} - T1_{b,h}\right) + W_{H_2,o}\, Cp_{H2}\,(T1_{o,h} - T1_{i,h}) \quad \ldots(7)$$

For TIP process (case7), the following heat equations are written as follow:

$$T1_{o,c} = \left(Q_{HE1} - W_{ln}\left(\lambda_{c1} + Cp_{c1,l}\left(T1_{b,c} - T1_{i,c}\right) + Cp_{c1,v}\, T1_{b,c}\right)\right)/(W_{ln}\, Cp_{c1,v}) \quad \ldots(8)$$

$$Q_{HE1} = W_{iso}\left(\lambda_{h1} + Cp_{h1,l}\left(T1_{b,h} - T1_{i,h}\right) + Cp_{h1,v}(T1_{o,h} - T1_{b,h}\right) \quad \ldots(9)$$

In this case (case 7) $T1_{i,h}$ doesn't equal to *T*.

Where:

$T1_{b,c}$&$T1_{b,h}$: Boiling temperature of cold and hot stream respectively, K

λ_{c1}&λ_{h1}: Latent heat of vaporization of cold and hot stream respectively, kj/kg

$Cp_{h1,l}$&$Cp_{c1,l}$: heat capacity of hot and cold stream respectively as liquid, kj/(kg k)

$Cp_{h1,v}$&$Cp_{c1,v}$: heat capacity of hot and cold stream respectively as vapor, kj/(kg k)

b) <u>Energy Balance of Heat Exchanger E_{202} (Figure 8a)</u>

This equipment is located before the stabilizer (Figure 10), where the hot stream is used to stabilize the isomerizate. Condensation of hot stream and vaporization of the cold stream are occurred based on heat exchanger1.

The area of heat transfer (A_{t2})is calculated as follow:

$$A_{t2} = \frac{Q_{HE2}}{U_2 \Delta T_{lm2}} \quad \ldots(10)$$

$$\Delta T_{lm2} = \frac{\Delta T_{2,1} - \Delta T_{2,2}}{ln\left(\frac{\Delta T_{2,1}}{\Delta T_{2,2}}\right)} \quad \ldots(11)$$

$$\Delta T_{2,1} = T2_{i,h} - T2_{i,c} \quad \ldots(12)$$

$$\Delta T_{2,2} = T2_{o,h} - T2_{o,c} \quad \ldots(13)$$

$$Q_{HE2} = W_{iso}\left(\lambda_{c2} + Cp_{c2,l}\left(T2_{b,c} - T2_{i,c}\right) + Cp_{c2,v}(T2_{o,c} - T2_{b,c}\right) \quad \ldots(14)$$

All parameters above are given as constant.

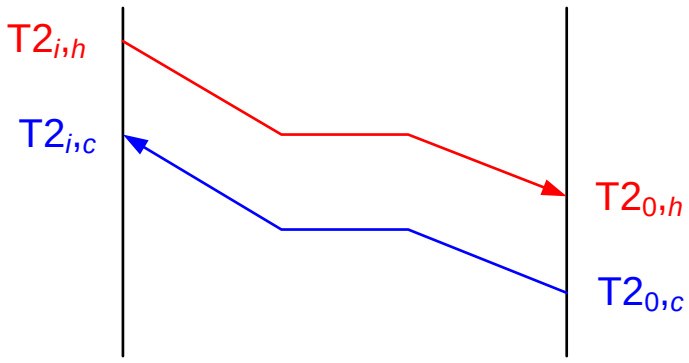

Figure 10: Heat exchanger E202

c) Energy Balance of Heat Exchanger E_{203} (Figure 8a)

The objective of energy balance is to obtain the heat transfer area (A_{t3}) and the amount of steam (W_{steam}) which can be described as follow:

$$A_{t3} = \frac{Q_{HE3}}{U_3 \Delta T_{lm3}} \quad \ldots(15)$$

$$\Delta T_{lm3} = \frac{\Delta T_{3,1} - \Delta T_{3,2}}{ln\left(\frac{\Delta T_{3,1}}{\Delta T_{3,2}}\right)} \quad \ldots(16)$$

$$\Delta T_{3,1} = T3_{i,h} - T3_{i,c} \quad \ldots(17)$$

$$\Delta T_{3,2} = T3_{0,h} - T3_{o,c} \quad \ldots(18)$$

$$T3_{0,c} = T2_{i,h} \quad \ldots(19)$$

$$T3_{i,c} = T2_{0,h}$$

…(78)

$$Q_{HE3} = W_{iso} Cp_{v,3} (T3_{o,c} - T3_{i,c}) \quad \ldots(20)$$

$$W_{steam} = Q_{HE3} / \lambda_{H2O} \quad \ldots(21)$$

This equipment is used to rise the bottom stream temperature of stabilizer by steam condensing as shown Figure 11.

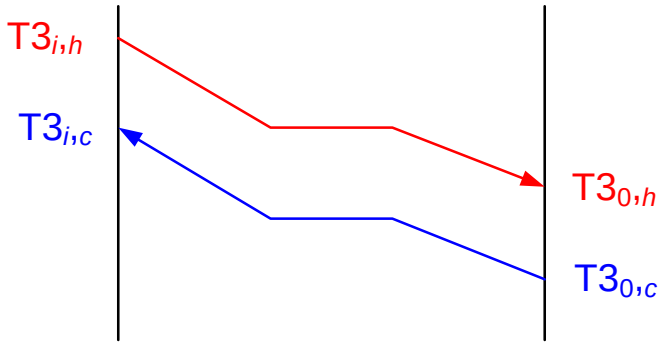

Figure 11: Heat exchanger E203

d) Energy Balance of Heat Exchangers E_{204} & E_{205} (Figure 8a)

These equipment (shown in Figure 12) works as coolers for stabilizing the isomerizate as E204, and light product of stabilizer (E205). Bellow, the equations of (A_{t4}) and cooling water rate (W_{H2O}) for heat exchanger4 (E204):

$$A_{t4} = \frac{Q_{HE4}}{U_4 \Delta T_{lm4}} \quad \ldots(22)$$

$$\Delta T_{lm4} = \frac{\Delta T_{4,1} - \Delta T_{4,2}}{ln\left(\frac{\Delta T_{4,1}}{\Delta T_{4,2}}\right)} \quad \ldots(23)$$

$$\Delta T_{4,1} = T4_{o,h} - T4_{i,c} \quad \ldots(24)$$

$$\Delta T_{4,2} = T4_{i,h} - T4_{o,c} \quad \ldots(25)$$

$$T4_{i,h} = T3_{0,h} \quad \ldots(26)$$

$$Q_{HE4} = W_{iso} Cp_{l,4} (T4_{i,h} - T4_{o,h}) \quad \ldots(27)$$

$$W_{H2O} = Q_{HE4} / (Cp_{H2O}(T_{i,H2O} T_{o,H2O})) \quad \ldots(28)$$

The same equations are used for E205.

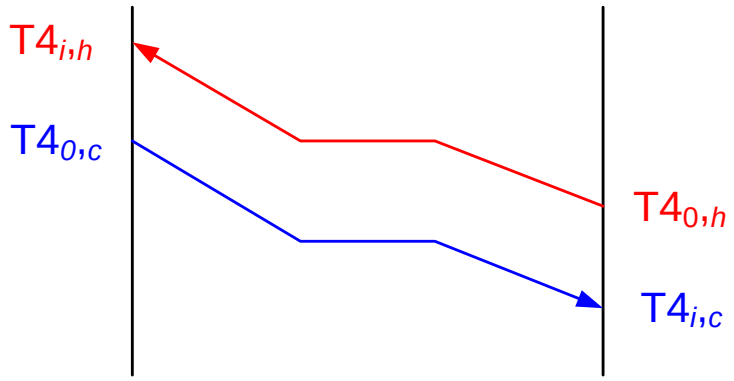

Figure 12: heat exchanger E204 and heat exchanger E205

e) Energy Balance of Heat Exchanger E_{206} (Figure 8a)

For the TIP process and the new process proposed here, heat exchanger E206 is used in addition to heat exchangers that are explained above.

$$A_{t6} = \frac{Q_{HE6}}{U_6 \Delta T_{lm6}} \quad \ldots(29)$$

$$\Delta T_{lm6} = \frac{\Delta T_{6,1} - \Delta T_{6,2}}{ln\left(\frac{\Delta T_{6,1}}{\Delta T_{6,2}}\right)} \quad \ldots(30)$$

$$\Delta T_{6,1} = T6_{i,h} - T6_{i,c} \quad \ldots(31)$$

$$\Delta T_{6,2} = T6_{o,h} - T6_{o,c} \quad \ldots(32)$$

$$T6_{o,c} = \left(Q_{HE6} - W_{ln}\left(\lambda_{c6} + Cp_{c6,l}\left(T6_{b,c} - T6_{i,c}\right) + Cp_{c6,v}\, T6_{b,c}\right)\right)/(W_{ln}\, Cp_{c6,v}) \quad \ldots(33)$$

$$Q_{HE1} = W_{iso}\left(\lambda_{h6} + Cp_{h6,l}\left(T6_{b,h} - T6_{i,h}\right) + Cp_{h6,v}\left(T6_{o,h} - T6_{b,h}\right) + W_{H_2,o}\, Cp_{H2}\left(T6_{o,h} - T6_{i,h}\right)\right) \quad \ldots(34)$$

$$T6_{i,h} = T \quad \ldots(35)$$

f) <u>Energy Balance of Furnace (F) (Figure 8a)</u>

The light naphtha stream is entered to the furnace in order to achieve the required reactor inlet temperature. Calculation of the furnace heat duty (Q_f) as a function of reactor inlet temperature is required to complete the cost model.

$$Q_f = (W_{ln} Cp_{f,v} + W_{H2} Cp_{H2})\left(T_{o,f} - T_{i,f}\right) \quad \ldots(36)$$

$T_{o,f}$& $T_{i,f}$: Outlet and inlet furnace temperature, K

$$T_{o,f} = T_i \quad \ldots(37)$$

$$T_{i,f} = T1_{o,c} \quad \ldots(38)$$

g) <u>Energy Balance of Furnaces (F_1 & F_2) (Figure 8a)</u>

As shown in the TIP flow sheet (Figure 7) instead of one furnace, there are two furnaces. Their heat duty (Q_{f1}&Q_{f2}) are calculated as follow:

$$Q_{f1} = (W_{ln} Cp_{f1})\left(T_{o,f1} - T_{i,f1}\right) \quad \ldots(39)$$

$T_{o,f}$& $T_{i,f}$: Outlet and inlet furnace temperature, K

$$T_{i,f} = T6_{o,c} \quad \ldots(40)$$

$$Q_{f2} = W_{H2} Cp_{H2}\left(T_{o,f2} - T_{i,f2}\right) \quad \ldots(41)$$

$T_{o,f2}$& $T_{i,f2}$: Outlet and inlet furnace temperature, K

The optimal kinetic parameters of the relevant reactions obtained by **Ahmed et al [1]** will be employed here to get the optimal operating conditions (temperature, pressure, LHSV, hydrogen ratio), which simultaneously will give the maximum RON, maximum yield and

minimum cost according to procedure shown in Figure 13 and using the following equations:

OBJ1 = Maximization of RON …(42)

OBJ2 = Maximization of *YIELD* …(43)

OBJ3 = Minimization of *OAUC* …(44)

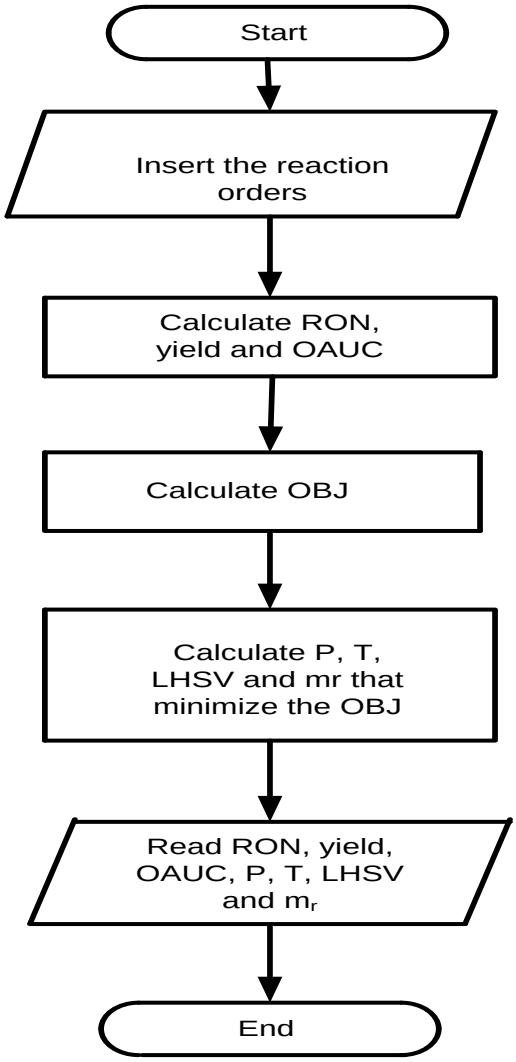

Figure 13: The procedure of isomerization configurations optimization

4.3 **Economic Cost Equations**

The cost estimation is necessary to complete the objective function of the optimization process for each unit (which is applied for all isomerization technologies including the new

AJAM process [1]. The overall annual cost of process is calculated by using the following relation [10, 11]:

Overall Annual Unit Cost (OAUC, $/yr)= Annual Unit Capital Cost (AUCC, $/yr) + Annual Unit Operating Cost (AUOC, $/yr) …(45)

The annual unit capital cost (*AUCC, $/yr*) are estimated from the total unit capital cost (*TUCC,* $*),* which represents the main equipments cost in the unit process such as reactor, heat exchanger, compressor, furnace, separator and pumps, as the following:

$$\textit{Annual Unit Capital Cost (AUCC, \$/yr)} = \textit{Total Unit Capital Cost (TUCC, \$)} \times \frac{\mathrm{i}\,(1+\mathrm{i})^{\mathrm{N}}}{(1+\mathrm{i})^{\mathrm{N}-1}} \quad \ldots(46)$$

The total unit capital cost (*TUCC, $*) can be estimated from the following equation [12]:

$$\textit{Total Unit Capital Cost (TUCC, \$)} = \textit{Installed Equipment Capital Cost (IECC, \$)} \times 1.45 \quad \ldots(47)$$

The installed equipment capital cost (*IECC,* $) is different from unit to another due to separation technology that are used. The following equation represents the installed equipment capital cost (*IECC,* $) for once through unit:

$$\textit{Installed Equipment Capital Cost (IECC, \$)} = \textit{Reactor Cost } (C_R) + \textit{Compressor Cost } (C_{co.}) + \textit{Heat exchanger Cost } (C_{HE})\ (1, 2, 3, 4\ \&\ 5) + \textit{Pumps Cost } (C_p) + \textit{Furnace Cost } (C_f) + \textit{Stabilizer Cost } (C_s)\ ) + \textit{separator cost } (C_s) \quad \ldots(48)$$

Annual unit operating cost (*AUOC,* $/yr) for each unit is calculated from the following equation:

Annual Unit Operating Cost (AUOC, $/yr) = Variable Unit Operating Cost (VUOC, $/yr) + Fixed Unit Operating Cost (FUOC, $/yr) …(49)

Variable Unit Operating Cost (VUOC, $/yr) = Heating Cost ($C_{Heat.}$) + Compression Cost ($C_{comp.}$) + Cooling Cost ($C_{cool.}$) + Catalyst Cost ($C_{cat.}$) + hydrogen consumption Cost (C_{H2}) + Pumping Cost ($C_{Pump.}$) + Steam Cost (C_{st}) …(50)

Fixed Unit Operating Cost (FUOC, $/yr)= Maintenance Cost ($f_1$)+ Operating Labour Cost (f_2)+ Laboratory Cost (f_3)+ Supervision Cost (f_4)+ Plant Overhead Cost (f_5)+ Capital Charge Cost (f_6) + Insurance Cost (f_7) …(51)

4.3.1 ***Installed Equipment Capital Cost (IECC, $)***

The economic cost of each equipment is estimated based on Marshal and Swift index as follow [10, 13, 14]:

a) <u>Reactor Cost (C_r)</u>

The reactor cost is calculated as a function to the length (L_r) and diameter (D_r) of the reactor, which are related to the liquid hourly space velocity (LHSV), as follow:

$$C_r = \left(\frac{M\ \&\ S}{280}\right) 101.9\ D_r^{1.066} L_r^{0.802}\ (2.18 + F_c) \quad \ldots(52)$$

$$F_c = F_m\ F_p \quad \ldots(53)$$

M&S is taken equal to 1622 [15].

F_c, F_m and F_p: dimensionless factors that are function of the operating pressure and material construction [6].

$$L_r = L + X \quad \ldots(54)$$

$$L = \sqrt[3]{\frac{4}{\pi}(L/D)\ V} \quad \ldots(55)$$

$$V = Q/LHSV \quad \ldots(56)$$

b) <u>Stabilizer Cost (C_s)</u>

The total distillation column cost is estimated as follow:

$$C_s = \text{Column Cost } (C_{col.}) + \text{Tray Cost } (C_{tray}) \quad \ldots(57)$$

Column cost calculated as a function to column length (L_c) and diameter (D_c):

$$C_{col.} = \left(\frac{M\ \&\ S}{280}\right) 101.9\ D_c^{1.066} L_c^{0.802}\ \ (2.18+F_c) \quad \ldots(58)$$

$$F_c = F_m\ F_p \quad \ldots(59)$$

$$C_{tray} = \left(\frac{M\ \&\ S}{280}\right) 97.24\ L_c\ D_c^{1.55}\ F_c \quad \ldots(60)$$

$$F_c = F_s + F_t + F_m \quad \ldots(61)$$

$D_c and\ L_c$ are calculated from the following equations [13]:

$$L_c = N_t(l_t + 1) \quad \ldots(62)$$

$$D_c = \sqrt[2]{\frac{4V_w}{\pi \rho_{vc} u_v}} \quad \ldots(63)$$

$$u_v = (-0.171 l_t^2 + 0.27 l_t - 0.047 \left[\frac{(\rho_{lc} - \rho_{vc})}{\rho_{vc}}\right]^{1/2} \quad \ldots(64)$$

Where:

V_w: maximum vapor rate, Kg/s

ρ_{vc}: vapor density, kg/m^3

ρ_{vl}: liquid density, kg/m^3

l_t: tray spacing, (m)

N_t: tray number, (-)

c) <u>Compressor Cost ($C_{co.}$)</u>

The compressor cost related to the reactor pressure is calculated as follow:

$$C_{co.} = \left(\frac{M\ \&\ S}{280}\right)(517.5)(bhp)^{0.82}(2.11 + F_d) \quad \ldots(65)$$

The compressor horsepower calculated as follow [16,17]:

$$bhp = hp\ /\ \eta_c \quad \ldots(66)$$

$$hp = \left(\frac{6.843 * 10^{-7}}{\omega}\right) P_{in} Q_{in} \left[\left(\frac{P_{out}}{P_{in}}\right)^{\omega} - 1\right] \quad \ldots(67)$$

$$\omega = \frac{\left(\frac{CP_{H2}}{CV_{H2}} - 1\right)}{\left(\frac{CP_{H2}}{CV_{H2}}\right)} \quad \ldots(68)$$

$$Cv_{H2} = Cp_{H2} - R \quad \ldots(69)$$

$$P_{out} = (P - P_{ns} y_{ns})/y_{H2} \quad \ldots(70)$$

d) Separator Cost (C_{sep})

$$C_{sep} = \left(\frac{M\&S}{280}\right) 937.63\ D_s^{1.066}\ L_s^{0.802} \quad \ldots(71)$$

D_s &L_s are the diameter and length of separator, which can be estimated as follows [15]:

To design the horizontal separator vessel, the estimation of the settling velocity of the liquid droplets is necessary.

For satisfactory separation, the required residence time (τ_r) = actual residence time(τ_a) …(72)

Required vapor residence time to settle the droplets to liquid surface (τ_r) is calculated as follow:

$$\tau_r = h_v/u_a \quad \ldots(73)$$

h_v: vapor high, m

u_a: settling velocity, m/s

$$h_v = 0.5D_s \quad \ldots(74)$$

$$u_a = 0.0105\sqrt{\frac{(\rho_{ln} - \rho_{H2})}{\rho_{H2}}}, \text{ (without demister)} \quad \ldots(75)$$

$$\tau_a = L_s/u_v \quad \ldots(76)$$

u_v: vapor velocity, m/s

$$L_s = 3D_s \quad \ldots(77)$$

$$u_v = Q_v/A_s \quad \ldots(78)$$

$$A_s = \frac{\pi}{4} D_s^2 \quad \ldots(79)$$

e) Pumps Cost (C_p)

Due to process flow sheet, there are two pumps, their cost are calculated with respect to naphtha mass rate as follows:

$$C_{Pump} = \left(\frac{M\&S}{280}\right) 9.84\times 10^3 F_c \left(\frac{Q_{pi}}{4}\right)^{0.55} \quad \ldots(80)$$

$$F_c = F_m\ F_p\ F_T \quad \ldots(81)$$

Q_{pi}: power of ith pump, kW

f) Heat Exchangers Cost (C_{HE})

The cost of heat exchanger related to reactor inlet and outlet temperature is calculated as follow:

$$C_{HE} = \left(\frac{M\&S}{280}\right) 210.78\ A_t^{0.65}(2.29+F_c) \quad \ldots(82)$$

$$F_c = F_m\ (F_d + F_p) \quad \ldots(83)$$

g) Furnace Cost (C_f)

$$C_{Furn.} = \left(\frac{M\&S}{280}\right) 5.52\times 10^3 Q_F^{0.85}\ (1.27+F_c) \quad \ldots(84)$$

$$F_c = F_m + F_p + F_d \quad \ldots(85)$$

h) Adsorber Cost (C_{ad})

Economic cost of adsorber column is calculated (for only process that use molecular sieve technology) as follow:

$$C_r = \left(\frac{M\ \&\ S}{280}\right)101.9\ D_r^{1.066} L_r^{0.802}\ (2.18+F_c) \quad \ldots(86)$$

$$F_c = F_m\ F_p \quad \ldots(87)$$

$$L = \sqrt[3]{\frac{4}{\pi}(L/D)\ V} \quad \ldots(88)$$

L/D: length to diameter bed ratio, (-)

V: bed volume, (m^3)

$$V = M_{5A}/\rho_{5A} \quad \ldots(89)$$

The ratio of l_d/D_d equals to 1.25 according to **Holcombe** [7].

The amount of catalyst (M_{5A}) is calculated by scaling down of the beds used in the scheme designed as shown below [6]:

Original	**This case**
33000 (kg of 5A)	18450(kg/hr of n-paraffins received)
M_{5A} (kg of 5A)	M_{np} (kg/hr of n-paraffins received)

The rate of normal paraffins received (M_{np}) is obtained by simulation process for each technology.

4.3.2 ***Fixed Unit Operating Cost (FUOC, $/yr)***

Each variable of fixed unit operating cost (FUOC) are estimated as follow [7, 10]:

- *Maintenance Cost (f_1):* It includes the cost of equipment spares and the cost of labour needed for the unit maintenance. Typically, the annual maintenance cost is taken (5-15%) of the installed capital cost.
- *Operating Labour Cost (f_2):* It includes the cost of the person needed to operate the plant. The value is taken 15% of the total annual operating cost.
- *Laboratory Cost (f_3):* It includes the desired laboratory analyses for process quality control. The value of laboratory cost is about 20 to 30% of the operating labour cost.
- *Supervision Cost (f_4):* It involves the direct supervision of operation and the management directly linked with operating the plant. The value is about 25% of the labour cost.
- *Plant Overhead Cost (f_5):* It involves all the general costs linked with operating the plant that are not involved with other headings (such as plant, offices, security, canteen, medical, safety and staff). This value are about (50-100%) of the labour cost.
- *Capital Charge Cost (f_6):* It is recovered as a depreciation charge. The value can be taken as 10% of the total unit capital cost.
- *Insurance Cost (f_7):* This value is often taken as (1-2%) of the total unit capital cost.

4.3.3 ***Variable Unit Operating Cost (VUOC, $/yr)***

The VUOC is calculated use the following equations:

a) <u>Compression Cost</u> ($C_{comp.}$)

The compressor can be estimated as follow based on the motor efficiency at 90% with a power price of 0.062$/kWh [16]:

$$C_{comp.}(\$/yr) = \left(\frac{bhp(hp)}{0.9}\right)\left(\frac{1kW}{1.341\ hp}\right)\left(\frac{0.062\$}{kWh}\right)\left(\frac{24h}{1\ day}\right)\left(\frac{342}{yr}\right) \quad \ldots(90)$$

b) <u>Heating Cost</u> ($C_{Heat.}$)

$$C_{Heat.}(\$/yr) = (Q_F(kW))\left(\frac{0.062\$}{kWh}\right)\left(\frac{24h}{1\ day}\right)\left(\frac{342}{1yr}\right) \quad \ldots(91)$$

c) <u>Pumping Cost</u> ($C_{Pump.}$)

$$C_{pump.}(\$/\text{yr}) = (Q_p(kW))\left(\frac{0.062\$}{kWh}\right)\left(\frac{24h}{1\ day}\right)\left(\frac{342}{yr}\right) \quad \ldots(92)$$

d) Cooling Cost ($C_{cool.}$)

It is calculated by the following equation with a price of cooling water (0.0035 $/kg) [17]:

$$C_{cool.}(\$/yr)= \left(W_{H2O}\left(\frac{kg}{h}\right)\right)\left(\frac{0.00175\$}{kg}\right)\left(\frac{24h}{1\ day}\right)\left(\frac{342}{yr}\right) \quad \ldots(93)$$

e) Hydrogen Consumption Cost (C_{H2})

It can be calculated by the following equation with a price of hydrogen at 0.49 $/$m^3H_2$ [18]:

$$C_{H2}(\$/yr) = \left(\frac{0.49\$}{m^3}\right)\left(\frac{m^3}{\rho_{H_2}kg}\right)\left(\frac{W_{H_2C}kg}{hr}\right)\left(\frac{24h}{1\ day}\right)\left(\frac{344}{yr}\right) \quad \ldots(94)$$

W_{H_2C}: weight rate of hydrogen consumption, (kg/hr)

$$W_{H_2,C} = W_{H_2,in} - W_{H_2,o} \quad \ldots(95)$$

M:total moles interred the reactor, mol

$$W_{H_2,in} = 2 * R * \frac{W_{ln}}{Mwt_{ln}} \quad \ldots(96)$$

$$W_{H_2,o} = 2 * y_{H2} * M \quad \ldots(97)$$

$W_{H_2,in}$ **&** $W_{H_2,o}$**:** weight rate of reactor inlet and outlet hydrogen, (kg/hr)

f) Catalyst Cost ($C_{cat.}$)

$$C_{cat.}(\$/\text{yr}) = (V\ m^3)\left(\frac{96\$}{kg}\right)\left(\frac{\rho_{cat}\ kg}{m^3}\right)\left(\frac{1}{t_{cat}\ yr}\right) \quad \ldots(98)$$

The catalyst price is taken 96$/kg [19], t_{cat} is the catalyst life time taken by 10 years [2].

g) Zeolite-5A Cost (C_{5A})

The price of 5A Iso-sieve Zeolite is equal to 2$/kg [19]

$$C_{5A} = (M_{5A})(kg)(\frac{2\$}{kg}) \quad \ldots(99)$$

h) Steam Cost ($C_{st.}$)

It is calculated by the following equation with a price of steam equals to 0.018 $/kg [20]:

$$C_{st.}(\$/yr)= \left(W_{st.}\left(\frac{kg}{h}\right)\right)\left(\frac{0.00259\$}{kg}\right)\left(\frac{24h}{1\ day}\right)\left(\frac{342}{yr}\right) \quad \ldots(100)$$

5. Performance Evaluation of Alternative Technologies

All the results have been obtained by using the feed stock composition presented in Table 5.

Table 5: Inlet and outlet composition of isomerization reactor which represents industrial data of Baiji North Refinery

Hydrocarbon components	inlet	outlet
n-Butane (nC4)	4.253	1.970
n-Pentane(nC5)	25.977	18.362
n-Hexane(nC6)	14.320	7.597
n-Heptane (nC7)	2.816	0.059
i-Butane (iC4)	0.353	0.963
i-pentane (iC5)	20.652	35.689
2,2 Di Methyl Butane (2,2DMB)	0.451	7.356
2,3 Di Methyl Butane (2,3DMB)	1.472	3.092
2 Methyl Pentane (2MP)	9.311	12.597
3 Methyl Pentane (3MP)	7.294	8.599
i-heptane (iC7)	5.084	0.250
Cyclo Pentane (CP)	1.312	1.369
Methyl Cyclo Pentane (MCP)	2.574	1.072
Cyclo Hexane (CH)	1.270	0.316
Benzene (C6)	0.433	0.000

5.1 **Optimal Case Studies**

Case Study 1: Once Through Process – Figure 1 (BNR)

The results presented in Table 6 show that the lowest RON (79.709) have been obtained from once through process because there is no normal paraffins recycle or branched paraffins by-pass is used which increasing the equilibrium conversion. Also, its cost (OAUC=10654036$) is low because owing to increase the equipment capacity and utilities due to the recycle used [3].

Table 6: Optimal operating conditions, economic and performance variables results of once through process (BNR Process)

Variables	Unit	Value
OAUC	$/yr	10653807
RON	(-)	79.452
Yield	(%)	97.683
T	K	524.31
P	MPa	2.4
LHSV	hr^{-1}	1.51
$\boldsymbol{m_r}$	mol H_2/ mol HC	3.31
CPU time	sec	0.718

Case Study 2: DIP Process (Figure 2)

From the results presented in Table 7 and in comparison with case once, adding of DIP to the base unit increases the RON (81.647) by 4.64% due to increase the normal pentane conversion, and OAUC (9390270$) was decreased by 11.83% owing to reduce the equipments sizes, hydrogen make up, catalyst amount, power and energy required because 20% of the feed stock have been separated before isomerizing it.

Table 7: Optimal operating conditions, cost and performance variables results of process with DIP

Variables	Unit	Value
OAUC	$/yr	9390270.0
RON	(-)	81.647
Yield	(%)	97.78
T	K	522.83
P	MPa	2.261
LHSV	hr^{-1}	1.402
$\boldsymbol{m_r}$	mol H_2/ mol HC	3.29
CPU time	sec	0.720

Case Study 3: DIH Process (Figure 3)

Based on the results shown in Table 8 and in comparison with case 1, increasing the RON (86.21) in this case leads to increase the OAUC (17249371$) due to increase the capital and operating cost as a result of increasing the feed stock by 26.36% in comparison with those obtained in once through process beside the cost of DIH process.

Table 8: Optimal operating conditions, cost and performance variables results of process with DIH

Variables	Unit	Value
OAUC	$/yr	17249371
RON	(-)	86.21
Yield	(%)	96.827
T	K	524.65
P	MPa	2.371
LHSV	hr^{-1}	1.429
$\boldsymbol{m_r}$	mol H_2/ mol HC	3.21
CPU time	sec	1.420

Case Study 4: DIP-DIH Process (Figure 4)

The results of this case are shown in Table 9. As proven and explained in case two, the use of DIP has a positive effect on the maximum RON and minimum cost. Using of DIP can

reduce the *OAUC* (16184704$) by 6.19% in comparison with case 3. Also the RON (88.292) increased by 2.082 compared with case 3 due to use DIP, so this feed stock composition and using of isomerization process with DIP and DIH technologies is preferred in comparison with the isomerization process with DIH.

Table 9: Optimal operating conditions, cost and performance variables results of isomerization process with DIP& DIH

Variables	Unit	Value
OAUC	$/yr	16184704
RON	(-)	88.292
Yield	(%)	97.51
T	K	523.4
P	MPa	2.373
LHSV	hr^{-1}	1.493
$\boldsymbol{m_r}$	mol H_2/ mol HC	3.847
CPU time	sec	0.281

Case Study 5: Ipsorb Process (Figure 5)

Total paraffins recycled are acquired with recycling 50% of the total normal paraffin in the feed stock leading to increase the reactor feed stock by 33% in comparison with once through process.

As shown in Table 10 and in comparison with case 1, the use of molecular sieve technique increases the RON (88.273) of isomerizate by 8.81, but such increases is associated with high *OAUC* (17641911$) due to high recycle rate although because the total paraffin recycled is acquired with recycling 50% of the total normal paraffin in the feed stock which leading to increase the reactor feed stock by 33% in comparison with once through process. Also, it is found that Ipsorb has the minimum OAUC in comparison with Hexorb and TIP process due to presence of DIP equipment which reduces the feed rate.

Table 10: Optimal operating conditions, cost and performance variables results of Ipsorb process

Variables	Unit	Value
OAUC	$/yr	17641911
RON	(-)	88.273
Yield	(%)	97.27
T	K	524.2
P	MPa	2.35
LHSV	hr^{-1}	1.419
$\boldsymbol{m_r}$	mol H_2/ mol HC	3.39
CPU time	sec	3.570

Case Study 6: Hexorb Process (Figure 6)

In Hexorb process (Table 11), the RON (90.04) has increased by 1.767 in comparison with Ipsorb process due to use DIH technique that increases the yield of 2,2DMB and 2,3DMB which have high RON. But such technique cause high increase in the feed stock as a result of methyl pentanes recycling and this scheme having the highest operating and capital cost. Although this technique gave the highest optimal value of RON compared with last technologies, such scheme exclusives to laboratory scale owing to its high OAUC (22886940$).

Table 11: Optimal operating conditions, cost and performance variables results of Hexorb process

Variables	Unit	Value
OAUC	$/yr	22886940
RON	(-)	90.04
Yield	(%)	96.89
T	K	522.9
P	MPa	2.382
LHSV	hr^{-1}	1.51
$\boldsymbol{m_r}$	mol H_2/ mol HC	3.412
CPU time	sec	0.717

Case Study 7: TIP Process (Figure 7)

As noticed from the results presented in Table 12 bellow, it has been observed that recycling 22 ton/hr of normal paraffins leads to increase the value of RON (88.17). This scheme has an economic cost (OAUC=19786370$) higher than Ipsorb process (17641911$) and lower than Hexorb process (22886510$). This behavior is attributed as follows: in Ipsorb process, the presence of DIP reduces the amount of recycled normal paraffins, while in Hexorb process, the presence of DIH increases the amount of recycled normal paraffins in addition to methyl pentanes recycle by DIH.

Table 12: Optimal operating conditions, cost and performance variables results of TIP process

Variables	Unit	Value
OAUC	$/yr	19786370
RON	(-)	88.17
Yield	(%)	97.06
T	K	521.72
P	MPa	2.317
LHSV	hr^{-1}	1.498
$\boldsymbol{m_r}$	mol H_2/ mol HC	3.18
CPU time	sec	1.388

Case Study 8: **AJAM** *Isomerization Process (Figure 8)*

The results of the recently developed **AJAM** process are presented in Table 13. The highest RON and highest yield are obtained by using this new configuration process in comparison with those obtained by traditional methods. Increasing in RON (90.81) (belong to the presence of benzene component in the final product that hydrogenated in others technologies. While, increasing the yield (99.20) belong to decrease the reactor feed stock rate by 48.34% weight percent than of once through process.

Table 13: Optimal operating conditions, cost and performance variables results of **AJAM** process

Variables	Unit	Value
OAUC	$/yr	15212319
RON	(-)	90.81
Yield	(%)	99.20
T	K	521.09
P	MPa	2.104
LHSV	hr^{-1}	1.503
$\boldsymbol{m_r}$	(-)	3.46
CPU time	sec	0.764

Also, the minimum OAUC required (15212319$) in comparison with others molecular sieve technologies is the lowest owning to reduce the feed rate leading to decrease the hydrogen make up, heating required, catalyst and all equipment capacities as shown in Table 14.

Table 14: AJAM, TIP and OT process comparison

Variables	AJAM Process	TIP	Once through
Reactor feed rate (Ton/hr)	40.6	101.27	75.841
Heating required (kW)	5033.5	7099.1	5652.38
Reactor bed volume (m^3)	39.25	89.64	74.20
Hydrogen make up (Ton/hr)	0.762	1.621	1.378

6. Energy Saving Opportunity in AJAM Process

Having found that AJAM process outweigh other existing isomerization processes (using same catalyst in the reactor), we look at the energy saving opportunity of the AJAM process based on pinch technology [21].

In order to develop a method of energy recovery and the best rearrangement of heat exchangers network, several efforts have been done in recent decay [22].

6.1 **Minimum Temperature Difference Calculation**

In case 8 and according to pinch theory, there are six streams: three hot streams need to cool and three cold streams need to heat. Each stream starts from temperature of source (T_s) and then cooled or heated to target temperature (T_t) as shown in Table 15. The heat capacity CP (kW/ºC) of each stream is given as follow:

$$CP = W * Cp \quad \ldots(101)$$

Where:

Cp: The heat capacity of stream, kJ/(kg.ºC)

W: mass flow rate of stream, kg/s

By using the data in Table 16 and following the procedure presented by **Linnhoff and Hindmarsh** [21], Figure 14 is plotted.

Table 15: Dimensionless factors values

	Dimensionless factors					
equipments	F_m	F_p	F_d	F_T	F_t	F_s
Reactor	3.67	1.275	-	-	-	-
Stabilizer column	3.67	1.12	-	-	-	-
Pump1	1	-	-	1	-	-
Pump2	1	1.5	-	1	-	-
Cooler1 &2	3.75	0.1	0.85	-	-	-
Heat exchanger1	3.75	0.25	0.85	-	-	-
Heat exchanger2	3.75	0.1	0.85	-	-	-
Heat exchanger3	3.75	0.1	0.85	-	-	-
Furnace	0.75	0.0	1	-	-	-
Pressure vessel	1	1.275	-	-	-	-
Tray (stabilizer)	1.7	-	-	-	0.0	1.4
Compressor	1	-	-	-	-	-

Table 16: Data required for heat integration problem

Stream number	**Type**	**CP (kW/ ºC)**			T_s,ºC	T_t,ºC	**Heat load**
		Vapor	λ/T_b	**Liquid**			
1	Hot	60.95	32.66	57.42	305	40	21446.4
2	Hot	48.09	-	-	305	250	2645
3	Hot	46.08	16	44.65	280	40	13877
4	Cold	60.32	32.66	57.2	40	305	23271
5	Cold	43.71	16	42.31	40	305	11703
6	Cold	13.98	-	-	70	305	3284

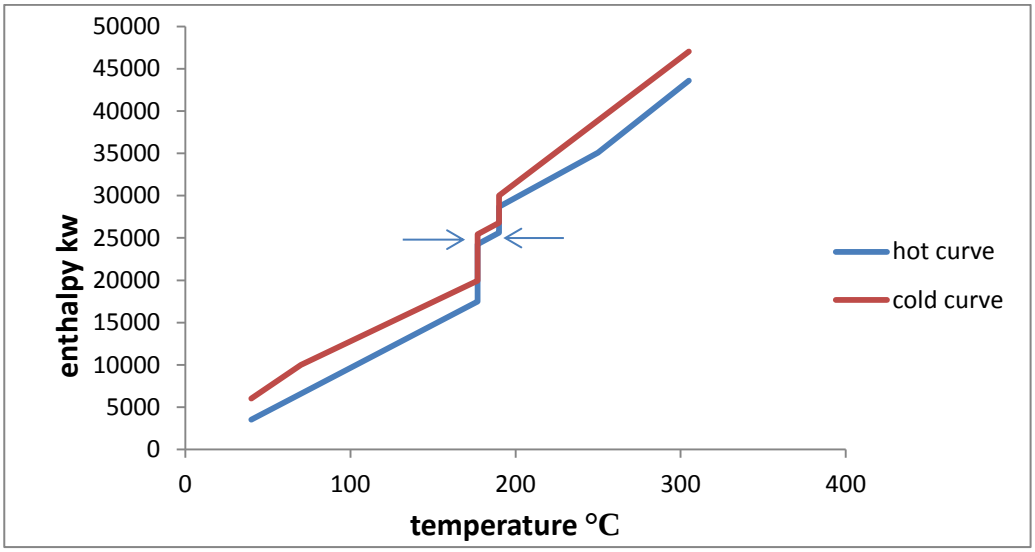

Figure 14: Cold and Hot streams composite curves

From plot of composite streams in Figure 14, the pinch acquires between 190ºC on the hot stream and 177ºC on the cold stream with minimum temperature (ΔT) difference equals to 13ºC.

6.2 **The Heat Exchanger Network Design**

The analysis carried out in Figure 14 has shown that the pinch can be occurred where the cold streams are at 177ºC and the hot 190ºC. Figure 15 shows the grid representation of the six streams, the dotted vertical lines represent the pinch and they separate the grid into two regions below and above the pinch [21].

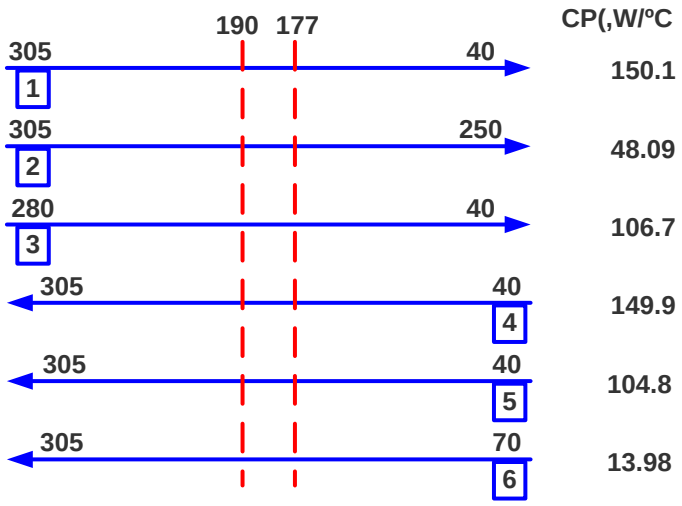

Figure 15: Grid of the six streams

The maximum recovery of energy is obtained if no cooling is utilized above the pinch. This means that the heat capacity of hot stream should be equal to or less than heat capacity of the cold stream above the pinch, and equals to or high than heat capacity of the cold stream below the pinch.

According to values of heat capacities, stream 1 is matched with stream 4, stream 2 is matched with stream 6 and stream 3 is matched with stream 5. Due to the equality of CP values for stream 1 with stream 4 and stream 3 with stream 5, same network design is used below and above the pinch. The heat duty is calculated by following equation:

$$Q_i = CP_v(T_s - T_b) + W\lambda + CP_l(T_b - T_t) \quad \ldots(102)$$

Where, *i* is the stream no.

Matching of steams 1 and 4, the following points are observed:

- ✓ The heat required to rise temperature of stream 4 from 40ºC to 305ºC equal to 21922.2kW
- ✓ The transferring heat required to bring stream 1 to 40ºC is equal to 21308.28kW.
- ✓ The transferring heat required to bring stream 1 to 53ºC is equal to 20461.40kW.
- ✓ Heating required for stream 4 =21922.2-20461.4=1460.8kW.
- ✓ Cooling required for stream 1=21308.28-20461.4=846.88kW.

Matching of steams 2 and 6, the following points are observed:

- ✓ The full amount of heat transferring from stream 2 to stream 6 is equal to 1883.64kW.
- ✓ The heat required to bring stream 6 to target temperature is equal to 3284.96 kW.
- ✓ Heating required for stream 6 =1401.36 kW.

Matching of steams 3 and 4, the following points are observed:

- ✓ The heat required to rise temperature of stream 5 from 40ºC to 305ºC equal to 14974.8 kW.
- ✓ The transferring heat required to bring stream 3 to 40ºC is equal to 13976.23 kW.
- ✓ The transferring heat required to bring stream 3 to 53ºC is equal to 13395.78 kW.
- ✓ Heating required for stream 5 =14974.8-13395.78=1579.02 kW.
- ✓ Cooling required for stream 3 =13976.23-13395.78=580.45 kW.

The results above are represented by the network presented in Figure 16.

According to the network shown above, the flow diagram of new process proposed (Fig. 8) is modified by adding a heat exchanger equipment before the second furnace (F202) reducing the heat duty supply to 6th stream in Figures (16 and 17) represent the modifying flow diagram of new isomerization proposed here.

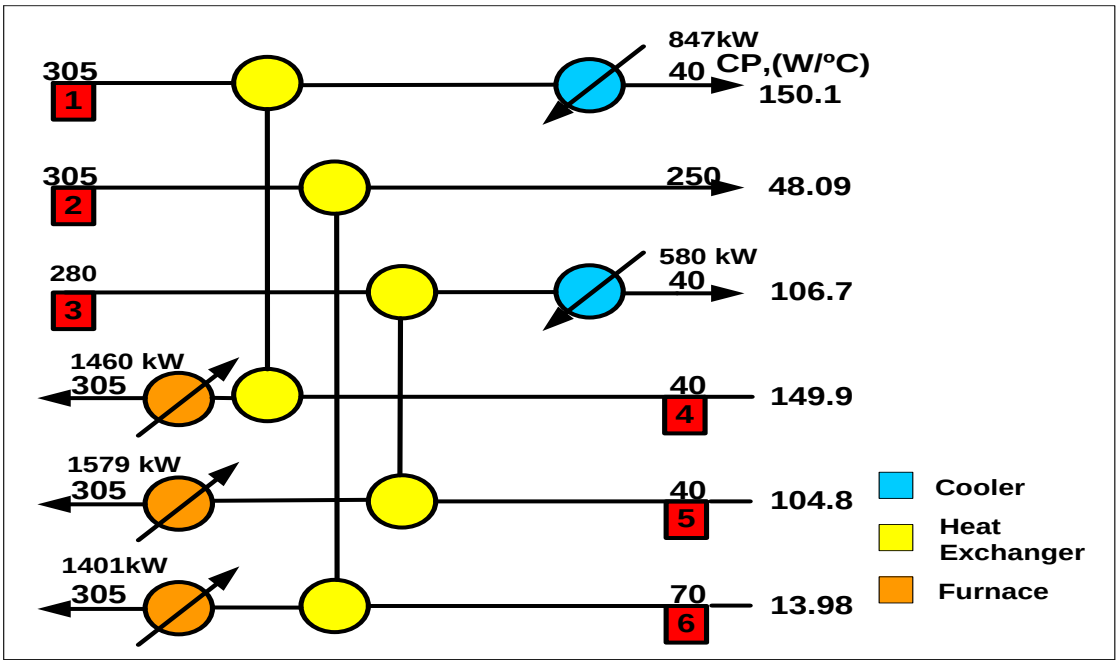

Figure 16: Proposed heat exchanger network for the new process proposed

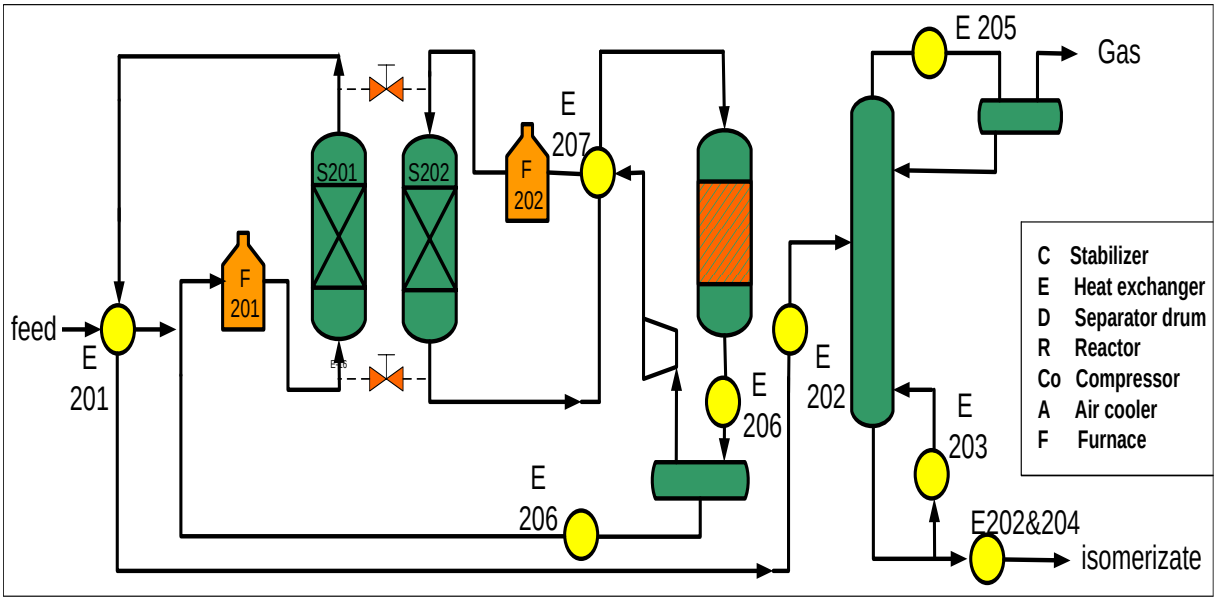

Figure 17: Modifying flow diagram of new isomerization process proposed

6.3 **Optimization Problem Formulation for Isomerization Configurations**

According to the equations (42 - 44) utilizing the mathematical model presented previously and applying the optimal kinetic parameter obtained in the last study [1], and using the flow diagrams showed in the previous section, the optimization problem of all cases are stated as:

Given	Initial concentration, kinetic parameters, reactor configuration, process specifications
Determine	Initial concentration, kinetic parameters, reactor configuration, process specifications
So as to	Maximise (RON & yield), Minimise OAUC
Subjected to	Process constraints and linear bounds on all decision variables.

The optimization problem for each isomerization technology is written as:

max OBJ

P, T, LHSV, m_r

s.t f(x(z),u(z), v) = 0 (model equation, equality constraint)

$P^L \leq P \leq P^U$ (inequality constraints)

$T^L \leq T \leq T^U$ (inequality constraints)

$LHSV^L \leq LHSV \leq LHSV^U$ (inequality constraints)

$m_r^L \leq m_r \leq m_r^U$ (inequality constraints)

6.4 **Case Study 9: Energy Saving of the AJAM Proposed**

Table 17 presents the optimal results of optimization problem that shows positive effect of heat exchanger E207 added. Where, the temperature difference has reduced by minimizing the OAUC owning to minimize the heating and cooling amount required in comparison with the results without heat integration. Also, the RON has slightly been increased owing to increase the temperature and decreasing the LHSV. The cost saving owning to use the heat integration process is 2.905% compared without heat integration as a result to reduce the total heating required by 11.465% and total cooling required by 8.94%. The new design achieved heat saving of 25.2% in comparison with the new configuration process of isomerization before making heat integration process.

Table 17: Optimal performance, cost and operating conditions of optimization problem for the AJAM process

Variables	Symbol	Unit	Value	
			With heat integration	Without heat integration
OAUC	*OAUC*	$/yr	14770103	15212319
Total heating required	Q_H	kW	4449.83	5027.4
Total cooling required	Q_C	kW	2736	3007
RON	RON	-	90.93	90.81
Isomerizate Yield	Yield	%	99.27	99.20
Initial temperature	T	K	520.84	521.09
Reactor pressure	P	MPa	2.11	2.104
LHSV	LHSV	hr^{-1}	1.460	1.503
H_2/HC mole ratio	m_r	-	3.37	3.46
Energy saving	E_s	**%**	**25.2**	

In order to assess the model parameters and providing sufficient evidence to ensure that values of model parameters evaluated do correspond to the global minimum of the objective function so that the developed process models is accurate, sensitivity analyses for *T, LHSV, P* and m_r values were performed. The information obtained from parametric sensitivity analysis is very useful for optimization and parameter estimation. It gives a clear indication which parameter has the largest impact on the accuracy of the model parameters. Sensitivity analysis is utilized for each of the estimated parameters by means of perturbations of the parameter value and is preferably in the range of ±10%, keeping the other parameters at their nominal values [11, 23]. For each perturbation in the parameter values, the objective function is re-calculated and then for each parameter the perturbation percentage is plotted against the corresponding value of the objective function as shown in Figure 18 for each parameter. When all the perturbations in all the model parameters give the same minimum of the objective function with their original values (0% perturbation), that means the global minimum has been achieved. From Figure 18, it is clearly noticed that the calculated model parameters are the optimum since at 0% perturbation the perturbations of *T, LHSV, P* and m_r give the same minimum of the objective function with their original values. Therefore, it is demonstrated that the global minimum has been achieved. It is also seen from this Figure that *T* and *LHSV* have the biggest influence on the model parameters compared to m_r and *P*.

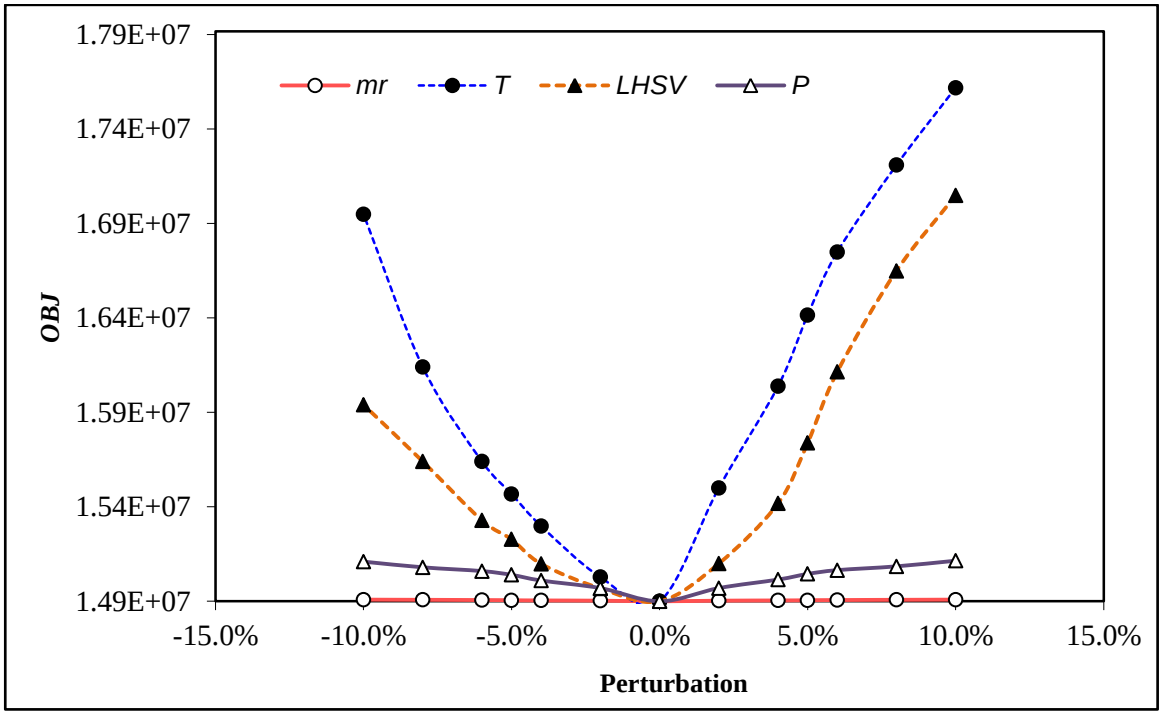

Figure 18: Sensitivity analysis of estimated model parameters for AJAM process

Comparison of different Isomerization Configurations (Cost Saving, Yield and RON)

The AJAM process gives the highest RON and yield with minimum cost. As presented in Table 18, a high cost saving verify by using the proposed configuration in a comparison with another configurations. The maximum cost saving is verified by 35% compared with Hexorb process, which had the maximum RON until this study. Also, beside the highest RON obtained by this study, this configuration gives the highest yield in comparison with all other technologies reported in such field.

Table 18: RON, yield and cost saving in AJAM process in comparison to different industrial isomerization processes

Parameters	AJAM Process	Hexorb	TIP	Ipsorb	DIH & DIP	DIH
Cost saving (%)	-	35.46	25.35	16.28	8.74	14.37
RON	**90.93**	90.04	88.17	88.273	88.292	86.21
Yield (%)	**99.27**	96.89	97.06	97.27	97.51	96.827

7. Conclusions

Several industrial isomerization technologies have been investigated in this study and optimized based on maximizing the RON and isomerizate yield, and minimizing of economic cost. It is found that the adding of DIP for each scheme has a positive effect on the RON, isomerizate and the operation cost. It is clearly observed that the recently proposed AJAM isomerization process gives the maximum RON, isomerizate yield and minimum economic cost in comparison to other molecular sieve technologies for the same feed stock and catalyst. The maximum cost saving (about 35%), highest RON (90.93) is obtained by using the **AJAM** process in a comparison to another existing industrial configurations. Also, beside the highest RON and cost saving obtained, the AJAM process gives the highest yield (99.27 %) in comparison to all other processes. Also, energy saving opportunity of the AJAM process was investigated using a pinch technology giving more than 25% savings in energy.

Nomenclature

Symbol	Description	Unit
A_s	cross section area of vapor flow rate	m^2
A_t	Total area of heat exchangers	m^2
A_{t1}	Area of heat of E201	m^2
A_{t2}	Area of heat of E202	m^2
A_{t3}	Area of heat of E203	m^2
A_{t4}	Area of heat of E204	m^2
A_{t5}	Area of heat of E205	m^2
A_{t6}	Area of heat of E206	m^2
A_{t7}	Area of heat of E207	m^2
AUCC	Annual unit capital cost	*$/yr*
AUOC	Annual unit operating cost	*$/yr*
bhp	horsepower required in the compressor	*Hp*
C_{Ad}	Adsorber capital cost	*$*
$C_{co.}$	Compressor Cost	*$*
$C_{comp.}$	Compression cost	*$*

$C_{col.}$	*Column Cost*	*$*
C_{cool}.	Cooling cost	*$/yr*
C_F	Furnace cost	*$/yr*
C_{H2}	Hydrogen concentration	mol/m^3
C_{HE}	Heat exchanger cost	*$*
$C_{Heat..}$	Heating cost	*$/yr*
C_i	Concentration of i^{th} component	mol/m^3
$C_{i,in}$	Initial (inlet) concentration of ith component	mol/m^3
$C_{pum.}$	Pumping cost	*$/yr*
C_{pump}	Pump cost	*$*
C_r	Reactor capital cost	*$*
$C_{sep.}$	*Separator cost*	*$*
C_{st}	*Stablization Cost*	*$*
C_{steam}	Steam cost	*$/yr*
C_{tray}	*Tray Cost*	*$*
C_{H2}	Hydrogen cost	*$/yr*
Cp	The heat capacity of streams	$kJ/(kg.^oC)$
$Cp_{i,p}$	Heat capacity of reaction product components	*J/mol.K*
$Cp_{i,r}$	Heat capacity of reaction reactant components	*J/mol.K*
Cp_m	Heat capacity of mixture	*J/(kg. k)*
Cp_{H2}	The specific heat capacity at constant pressure	*J/(kg. k)*
$Cp_{h1,l}$	heat capacity of hot stream as liquid in E201	*kJ/(kg k)*
$Cp_{c1,l}$	heat capacity of cold stream as liquid in E201	*kJ/(kg k)*
$Cp_{h1,v}$	heat capacity of hot stream as vapor in E201	*kJ/(kg k)*
$Cp_{c1,v}$	heat capacity of hot and cold stream respectively as vapor in E201	*kJ/(kg k)*
d_t	Tube diameter	m
D_{Ad}	Adsorber diameter	*(m)*
D_c	column diameter	(m)
D_r	Reactor diameter	
F_m , F_p, F_d	Dimensionless factors that are function of the material construction, operating pressure and design, respectively	(-)
G	raw material flow rate	m^3/hr^{-1}
h_v	Vapor high	*m*

hp	the isentropic compressor horsepower	Hp
i	hydrocarbon components number	(-)
j	Reaction number	*(-)*
l_t	Tray spacing	m
L	Reactor bed length	m
L_{AD}	Adsorber length	m
L_c	Column (stabilizer) length	m
L_r	Reactor length	m
L_s	Separator length	m
$LHSV$	Liquid hourly space velocity	hr^{-1}
m_r	Mole ratio of hydrogen to light naphtha	(-)
N_t	Number of tray	(-)
P	Reactor pressure	Pa
Pin , P_{out}	Inlet and outlet pressure in the compressor	Pa
P_{ns}	Naphtha stream pressure	Pa
q_F	Furnace heat duty	kJ/rh
q_{E201}	rate of heat transfer through E201	kJ/rh
q_{E202}	rate of heat transfer through E202	kJ/rh
q_{E203}	rate of heat transfer through E203	kJ/rh
q_{E204}	rate of heat transfer through E204	kJ/rh
q_{E205}	rate of heat transfer through E205	kJ/rh
q_{E206}	rate of heat transfer through E206	kJ/rh
q_{E207}	rate of heat transfer through E207	kJ/rh
q_p	power of the pump	kJ/hr
Q_{in}	Flow rate of hydrogen at compressor section	m^3/hr
Q_{ln}	Liquid Flow rate of light naphtha	m^3/hr
Q_v	Hydrogen volumetric flow rate	m^3/hr
RON	Research octane number	(-)
$T1_{b,c}$	Boiling temperature of cold and stream in E201	K
$T1_{b,h}$	Boiling temperature of hot stream in E201	K
$T1_{i,h}$	The inlet temperature of hot stream into E201	K
$T1_{i,c}$	The inlet temperature of cold stream into E201	K
$T1_{o,h}$	The outlet temperature of hot stream from the E201	K
$T1_{o,c}$	The outlet temperature of cold from E201	K

$T_{o,F}, T_{i,F}$	Outlet and inlet furnace temperature	*K*
u_a	settling velocity	*m/s*
u_v	Vapor velocity	*m/s*
U_1	Heat transfer coefficient of E201	*kJ/(m^2.K.hr)*
U_2	Heat transfer coefficient of E202	*kJ/(m^2.K.hr)*
U_3	Heat transfer coefficient of E203	*kJ/(m^2.K.hr)*
U_4	Heat transfer coefficient of E204	*kJ/(m^2.K.hr)*
U_5	Heat transfer coefficient of E205	*kJ/(m^2.K.hr)*
U_6	Heat transfer coefficient of E206	*kJ/(m^2.K.hr)*
U_7	Heat transfer coefficient of E207	*kJ/(m^2.K.hr)*
V_{Ad}	Adsorber bed volume	*m^3*
V_w	Maximum vapor rate	*kg*/s
W_{5A}	Weight of 5A zeolite catalyst	*kg*
$W_{cat.}$	Weight of 5A zeolite catalyst	*kg*
W_{H2}	Weight flow rate of hydrogen inter to reactor	*kg/hr*
$W_{H2,\,C}$	weight rate of hydrogen consumption	*kg/hr*
$W_{H2,in}$	weight rate of hydrogen inlet to the reactor	*kg/hr*
$W_{H2,o}$	weight rate of hydrogen out from the reactor	*kg/hr*
W_{H2O}	Weight flow rate of cooling water	*kg/hr*
W_{ln}	Weight flow rate of light naphtha	*kg/hr*
W_{steam}	Weight flow rate of steam	*kg/hr*
X	Inert bed high	*m*
y	Mole fraction	(-)
Z	Compressibility factor	(-)

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Appendix A

Table A1: Mathematical modelling equations

Mass balance equation:

$$G\frac{dCi}{dV} = \sum_{j=1}^{m} a_j . r_j$$

Energy balance equation:

$$G\frac{dT}{dV} = \frac{1}{\rho\ C_p^m} \sum\nolimits_{j=1}^{m} Q_j . a_j . r_j$$

Reaction rate equations:

$$r_j = \eta_j k_j\ C_i^n$$

$$k_j = A_j \exp\left(\frac{-E_j}{R\ T}\right)$$

$$C_i = (y_i\ p\ )/(Z_i\ R\ T)$$

Effectiveness factor

$$\eta_j = \frac{\tanh\varphi_j}{\varphi_j}$$

$$\varphi = \frac{V_P}{S_P}\sqrt{\left(\frac{n+1}{2}\right)\left(\frac{r_j\ C_i^{-1}\ \rho_p}{D_{e,i}}\right)}$$

Effective diffusivity:

$$D_{e,i} = \frac{\epsilon_S}{\mho}\frac{1}{\frac{1}{D_{mi}^g}+\frac{1}{D_{ki}}}$$

$$\mho = \frac{1 - 0.5log\varepsilon_s}{\epsilon_s}$$

$$D_{ki} = 349200\ r_g\sqrt{\frac{T}{MW_i}}$$

$$D_{mi}^g = (1 - yi)1/\sum_{k\neq i}^{NCG}\frac{y_k}{D_{i,k}}$$

$$D_{i,k} = 188.2458{*}10^{-20}\sqrt{T^3\left(\frac{1}{MW_i}+\frac{1}{MW_k}\right)} * \frac{1}{P\ \sigma_{i,k}^2\ \cap_D}$$

$$\sigma_{i,k} = \frac{\sigma_i + \sigma_k}{2}$$

$$\sigma_i = 1.18 * 10^{-9}(V_{bi})^{\frac{1}{3}}$$

$$\cap_D = \frac{1.06036}{(T^*)^{0.1561}} + \frac{0.193}{\exp(0.47635T^*)} + \frac{1.03587}{\exp(0.01529T^*)} + \frac{1.76474}{\exp(3.89411T^*)}$$

$$T^* = \frac{T}{\varepsilon_{ik}/C_B}$$

$$T_{c,ik} = \sqrt{T_{ci}T_{ck}}$$

$$\varepsilon_{ik}/C_B = 0.75T_{c,ik}$$

Equations of RON estimation:

$$RON = \sum_{i=1}^{m}(RON_i . y_i) + \beta$$

$$\beta = \frac{1}{100}\sum_{i=1}^{m-1}\sum_{j=2}^{m}\beta_i\beta_j y_i y_j$$

$$\beta_i = \alpha\left(\frac{Di_i}{Di_{max}}\right)^{\gamma}$$

Yield calculation equation:

$$Yield = M_{iso}/M_{ln}$$